



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

TRANSACTIONS.

THE Kansas Academy of Science met in its nineteenth annual session in the rooms of the State Normal School, at Emporia, the meeting opening on the afternoon of the 17th, and continuing through the 18th and 19th of November, 1886. Papers accepted by the committee on publication appear in the following pages.

The election of officers for the following year resulted as follows:

President—J. D. Parker.

Vice Presidents—J. R. Mead, E. H. S. Bailey.

Secretary—E. A. Popenoe.

Treasurer—I. D. Graham.

Curators—F. W. Cragin, L. L. Dyche, D. S. Kelly, N. S. Goss, A. H. Thompson.

Librarian—F. W. Cragin.

The address of the first evening session was given by Dr. John C. Branner, of the University of Indiana, upon the subject, "Geologists, Professional and Unprofessional;" of the second evening session by the retiring President of the Academy, Prof. E. L. Nichols, of the University of Kansas, upon "The Sky." At the various sessions the following papers, among others, were read:

ON BLACK AND WHITE.

BY EDWARD L. NICHOLS, PH. D.

In the spectrophotometric study of pigments, the selection of a suitable standard of color is of considerable importance. The ideal standard would be a body which reflects all wave-lengths of the visible spectrum equally well; but in practice this normal white cannot be obtained, and it becomes necessary to adopt as a working standard some substance which gives a fair approximation to the normal white, and having selected this, to determine as accurately as possible its variations from that standard.

It is my object in the present paper to describe some determinations of the character of certain pigments which had been selected as standard whites in the spectrophotometric analysis of color. The mere inspection of white pigments with the unaided eye brings to view marked differences of tint, the existence of which is for the most part unknown except to those who have had occasion to make careful comparisons of such substances; and these differences are sufficiently pronounced to lead to the rejection of all but a very few substances on the part of one seeking for a standard white. Of these few, even the best are far from satisfactory, and I have found none which, to the unaided eye, approaches more nearly the ideal standard than the carbonate of magnesium. The oxide of the same metal, which when prepared by burning magnesium ribbon or wire, gives a very brilliant white, loses splendor when taken in bulk, and appears at a decided disadvantage when compared with the carbonate.

The carbonate of magnesium possesses the advantage of cheapness, and it may

be obtained commercially in cubes or rectangular blocks of convenient size and the requisite degree of firmness, the surfaces of which are easily removed by scraping as often as they become soiled. These advantages, coupled with the fact that it appeared to the eye to be a very nearly perfect white, led to its adoption as a working standard in my spectrophotometric study of pigments¹ and of the color of the sky.²

An inspection of different commercial specimens of the carbonate, placed side by side, discovered such differences of tint as to make it impossible to select the one most suitable for a standard. The tendency is in such a case, to accept as white the one presenting the most brilliant appearance, and to regard all others by comparison as yellowish or creamy, just as one is apt unconsciously to adopt the sharpest of a series of musical tones of nearly the same pitch as the standard, and to regard the rest as flat.

In either case the result of the comparison is almost sure to be misleading. It becomes necessary, therefore, to subject the specimens to a careful spectrophotometric analysis, and to adopt that one as standard which shows the least deviation from the true white.

This determination is a matter of considerable difficulty. It involves the comparison, wave-length for wave-length, of the spectrum of the light reflected by the pigment, with the direct spectrum of the light illuminating it. The intensities of the direct and reflected spectra are so very different as to make this comparison exceedingly unsatisfactory. Any reduction of the intensity of the direct spectrum, by means of absorbing media or by reflection, is inadmissible, since we have no substance at command which will absorb or reflect different wave-lengths in precisely the same proportion. The use of a revolving disk with slits of adjustable width might be regarded by some as free from objection; but it is a matter of serious question whether the comparison of an intermittent ray with a persistent ray, even of the same wave-length, is in any degree trustworthy.

A source of error, unavoidable in any form of spectrophotometer, viz., slight modifications on the one hand by selective absorption and reflection in the Nicols prisms and on the other hand in the prisms or mirrors by means of which the unpolarized ray is brought to the slit of the collimator, cannot be eliminated. But these effects are fortunately small, and may be allowed for when their amount has been approximately determined. In the choice of the source of illumination one is limited to diffuse daylight, which is unfortunately subject to most perplexing fluctuations in intensity and quality alike, and to the use of the gas or petroleum flame or of the incandescent electric lamp — sources which, at their best, have little to be desired in the matter of constancy, but which are of such small intensity and so low in temperature as to seriously affect the accuracy of the comparison, even in the brightest parts of the spectrum, and to render it impossible to carry the measurements much beyond the neighborhood of the G line. In spite of these disadvantages, I found that the most trustworthy results were to be obtained by making comparison in an otherwise dark room, using as the sole source of illumination the flame of a "bat's-wing" gas burner.

The spectrophotometer used in these measurements was of the form described in the researches mentioned in a previous paragraph. In this instrument the spectra to be compared are brought into vertical juxtaposition in the eye-piece of an ordinary one-prism spectroscop, equal wave-lengths in the tube being everywhere in the same vertical straight line. The brighter of the two spectra was polarized by

¹ American Journal of Science. Vol. 28, Nov., 1884.

² Proceedings of the American Association for the Advancement of Science, Ann Arbor meeting, 1885. Vol. 34, p. 78.

passing the ray through the two nicols in front of the slit, the first of which was free to revolve, while the second was fixed with the longer diagonal of its faces parallel to the slit. By revolution of the first nicol this spectrum could be given any desired intensity, from that which it possessed when the polarizing planes of the two nicols were parallel, to zero, when the nicols were in position of extinction. The intensity of this spectrum was indicated by a finger attached to the movable nicol, which finger moved over a graduated circle. The ray producing the other spectrum, reflected from the surface of the pigment to be tested, entered the slit by total reflexion from the surface of a small, right-angled prism, the edge at one of the acute angles of which was at right angles to and in contact with the middle of the slit. In other respects, the instrument was an ordinary, one-prism spectroscop, into the eye-piece of which had been inserted a diaphragm containing a small, narrow, vertical slit.

If such an instrument be set up in front of a gas flame, so that the direct rays of the flame will form the polarized spectrum, and the pigment, the whiteness of which is to be tested, be placed above the reflecting prism at the slit so that its surface is illuminated by the same flame, and by that alone, certain of the rays reflected by the pigment will enter the upper half of the slit and form the unpolarized spectrum.

Were this pigment a true white, the reduction of the direct spectrum necessary to render these spectra equally bright would be precisely the same throughout their entire length. Any deviation from true whiteness manifests itself by undue brilliancy or weakness of some components of the light reflected by the pigment.

The amount of this variation may be measured, moreover, by going through the spectrum from end to end and noticing for each wave-length the position of the movable nicol at which that particular ray from the direct flame equals in intensity the corresponding ray reflected by the pigment. The spectrum of the pigment under these circumstances was very faint, but by taking the precaution to guard the retina throughout the experiment from the fatigue which follows exposure to even moderately bright objects, it was found possible to obtain a series of comparisons of the reflexion spectrum of a block of magnesium carbonate with the direct spectrum of the flame illuminating it.

To avoid even the loss of sensitiveness of the eye involved in reading the position of the movable nicol, it was necessary for two persons to take part in the measurements, one observing at the eye-piece of the instrument and keeping his eyes constantly in the rested condition upon which accurate settings so much depended, while the other moved the rotating nicol to the position indicated by the observer, read off that position and the wave-length to which the reading corresponded, made the necessary notes, and kept the apparatus in proper adjustment. This plan served another very important end. The movement of the Nic-

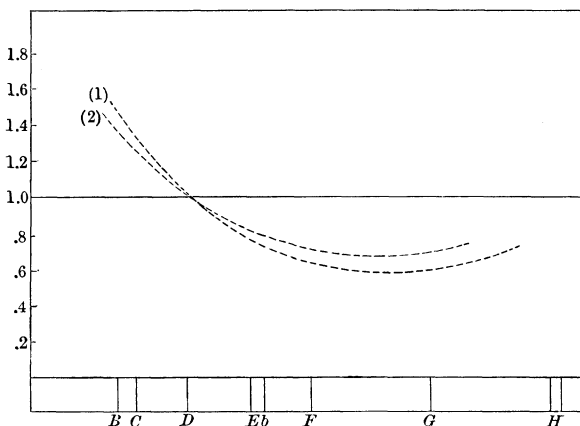


FIGURE I.—Intensity curves of two specimens of Magnesium Carbonate

ol's prism necessary to bring about the equality of the two spectra was out of the direct control of the observer, who thus relied upon his visual perception, entirely unbiased by the knowledge that the setting which he was directing his assistant to make differed in this respect or that from a looked-for result. The advantage of such an arrangement in work of this kind is very great. The personal equation in photometry of all kinds is very large, and in the photometry of the spectrum it is especially troublesome.

To further eliminate the personal element, my assistant, Mr. W. S. Franklin, duplicated nearly every series of observations. The result of our measurements upon the reflexion spectrum of this block of magnesium carbonate is shown in Curve I, Figure I. Abcissæ are wave-lengths, the spectral regions being denoted by the positions of the chief Fraunhofer lines. Ordinates are intensities, that of the region of the D line being taken as unity. A true white possessed of the same reflecting power as this block of magnesium carbonate would have as its curve of intensities the horizontal dotted line shown in the figure. Deviations from this line indicate, for each portion of the spectrum, the variation of the pigment from true whiteness. It will be seen from the figure that this specimen reflected a greater proportion of the red and less of the wave-length shorter than D than a true white would have done. Another specimen of the same substance gave a curve of quite the same character, No. 2, Fig. I. Its color, in a word, was a red of an exceedingly small degree of saturation, and the inspection of other whites has led me to the conclusion that the same peculiarity is common to most white pigments, excepting when viewed in very thin films. The curve of this specimen of magnesium carbonate once obtained, the measurement of others was a comparatively easy matter. This specimen was used as a working standard, with which the pigment to be measured could be compared.

A comparison of several other white substances revealed the presence of blue adulterants. The addition of a very small quantity of ultramarine or indigo compensates for the preponderance of the longer wave-lengths in the spectrum of these pigments, and adds greatly to their brilliancy.

The intensity curves of specimens of white paper, of plaster of paris prepared for dentists' use, and of carbonate of magnesium, show, unmistakably, the presence

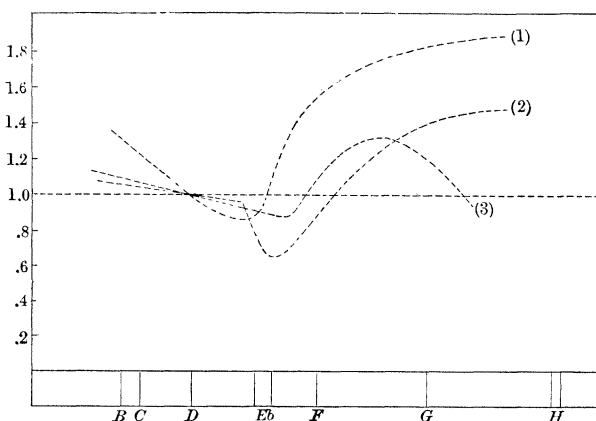


FIGURE II.—Intensity curves of adulterated whites.

(1) Plaster of Paris. (2) Magnesium Carbonate. (3) Paper.

of this blue coloring matter. Although to the naked eye the only effect was increased brilliancy of tone, the adulteration unfits the substance altogether for use as a standard white. These curves are shown in Figure II. The reflexion spectrum of the paper possesses a well-marked maximum between the Fraunhofer lines F and G, while the intensity of the rays be-

yond the G falls off to an amount less than that belonging to a true white. The

coloring matter used in this specimen is probably indigo, but the plaster of paris and magnesium carbonate were undoubtedly colored with ultramarine, in consequence of which the entire violet end of the spectrum is much brighter than in a true white. Thus the spectrophotometer affords a means of showing the presence of such coloring matters in quantities much too minute to be detected in any other way.

The preponderance of the longer wave-lengths in the spectrum of unadulterated white pigments is not due to selective reflexion, but is produced by absorption of the more refrangible rays in process of transmission, so that those portions of the light which penetrate to a considerable depth and are reflected internally, acquire a very decidedly reddish tone, which although diluted by mixture with the unmodified light reflected at the surface, gives the creamy tint common to such substances. That this is true can often be shown by coating a piece of glass with the substance in question in the form of powder. Such a coating, when of considerable density, is found to transmit light of a strong orange or red color, which disappears whenever the coating becomes sufficiently thin. The appearance of such coatings by reflected light shows the modification due to the admixture of the red rays reflected internally, sometimes in a very striking manner, and the color, as the coating becomes thinner and thinner, invariably tends toward blue. In the case of some substances, notably

of the well-known blowpipe films of antimony oxide, the blue appearance is very pronounced. The spectrophotometric analysis of these blue films and of the blue precipitate in very dilute opalescent solutions—for instance, the solution of hypsulphate of soda from which the sulphur has been precipitated by an acid—led to a surprising result. The fumes of antimony before

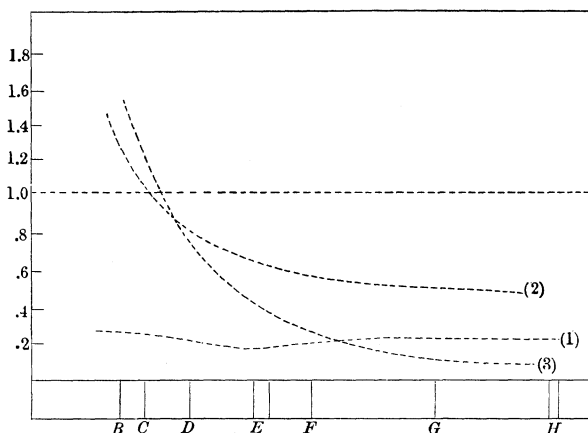


FIGURE III.—Intensity curves of the spectrum of Antimony Oxide.

- (1) Reflexion spectrum of a thin film. (2) Reflexion of a thick film.
(3) Absorption spectrum of a thick film.

the blowpipe, having been caught upon the surface of a pane of white glass, showed when viewed by reflected light the usual appearance of a white film shaded off by insensible gradations, as the coating became thinner, to a delicate sky-blue. By transmitted light the thicker portions of this film were orange, the color disappearing until in those parts which presented a blue appearance by reflected light, no absorption effect could be detected.

The absorption spectrum of the denser part of this film and the reflexion spectra of the thickest and thinnest portions were subjected to a photometric analysis.

The result is shown in Fig. III.

The thin film, in spite of its unquestionably blue appearance to the unaided eye, gave a very faint spectrum in which no excess of blue or violet rays could be detected with certainty, the energy curve approaching more nearly that of a true white than did the curve of any so-called white pigment which I have investigated.

The excess of blue and violet in this case, if such existed, was certainly very much less marked than in the adulterated whites already mentioned. The thick portions of the same film which were accepted by the eye as being of unusually pure whiteness, showed the influence of the absorption of the shorter wave-lengths, and the absorption spectrum of the same portion possesses a curve in which the red end of the spectrum is at least thirty times brighter than the region midway between the G and H line.

It seems evident, from this result, that we have to do in the antimony film with a so-called *subjective blue*; with a color, in other words, which does not arise from any marked excess of violet rays; and I believe the antimony film to be in this respect typical of a very large class, viz., of all opalescent media. I am aware that this view is not in accordance with those generally held concerning opalescence, it being generally supposed that in such substances the incident ray is selectively divided into two components, one of which, containing an excess of the longer wave-lengths, gives the film its ruddy appearance when viewed by transmitted light, while the blue appearance by reflected light is to be ascribed to the quality of the reflected rays.¹

It is commonly maintained that the particles of which such films are composed reflect blue light and transmit the red because of their small size. I have long regarded this explanation as unsatisfactory, and the analysis of the reflexion and absorption spectra just described, which constitutes, I believe, the first attempt to measure spectrophotometrically the light reflected and transmitted by an opalescent medium, affords us evidence that these substances *reflect* all visible rays equally well, *absorb* the shorter wave-lengths, and transmit a corresponding excess of red light.

I have assured myself, moreover, by an inspection of the antimony films under the microscope, with properly-managed illumination from above, that the particles of those portions of an antimony film which appear blue to the unaided eye, though small, are capable of reflecting white light. Under such circumstances all traces of blue vanish, and the field of view shows the particles of antimony oxide, of a pure white, very sparsely distributed upon a black background. These particles, which are readily measured by means of the eye-piece micrometer, vary in diameter from .0007 millimeters to .0015 millimeters; and portions of the same film, when thick enough to appear perfectly white to the naked eye, present in the microscope a field in which the particles are of the same sizes and of the same individual appearance, but in which the number per unit of area is much greater.

The hypothesis that the differences of color in such films are due to differences in the size of particles, can, moreover, be disposed of by the following very simple but conclusive experiment: If antimony be burned in the flame of a blast lamp and a piece of smoked glass or charcoal be exposed for an instant to the fumes, the thin film first formed will present the color usually obtained before the blowpipe, and it may be converted into the white film by a longer exposure. In this case, the change of color is produced by the accumulation of the same particles which, at the beginning of the experiment, went to build up the blue film, and the change in appearance cannot be ascribed to any arrangement in order of sizes upon different portions of the glass, but is evidently due to the increasing thickness of the deposit.

A spectrophotometric analysis of the opalescent solution produced by precipitating sulphur from a solution of hyposulphite of soda gave results similar to those obtained with the antimony film. The sulphur precipitate, as is well known, presents by reflected light, in its incipient stages, a blue color quite as striking as that of the antimony film. This changes to a milky white as the precipitate becomes

¹ See C. H. Kayle, Am. Journal of Science.

denser; and the solution, in which at first no selective absorption can be noticed, transmits, as the experiment proceeds, light in which red and yellow become more and more dominant.

Fig. IV shows the intensity curves of the reflexion spectrum of the hyposulphite solution in its blue stage and in the milky stage, also the absorption spectrum of the latter.

In the same figure is given, for purpose of contrast, an intensity curve obtained from artificial ultramarine, the result of measurements which have been already published.¹

It will be seen upon inspection of these curves, that the sulphur precipitate, even in its first stages, shows no measurable excess at the violet end of the spectrum; that this curve differs from the denser precipitate only in intensity; and that both curves represent within narrow limits the spectrum of the true white.

The absorption spectrum of this solution (Curve 3) shows a decided excess in the red and yellow, and an equally unmistakable deficiency toward the violet.

The appearance of a pronounced and very beautiful blue in substances which reflect light of an almost pure white is, I believe, by no means confined to the cases under considera-

tion here. Two important factors in the production of these subjective blues may be briefly referred to. In the first place, we unconsciously adopt as our standard of whiteness, light reflected by pigments which are really of a decidedly yellow-reddish tone. The excess of yellow and red in the ordinary so-called whites of every-day life leads us to the adoption of this false standard, because, with the probable exception of snow, all white substances with which we have to do possess this peculiarity.

Any substance reflecting all wave-lengths in the same proportion will be regarded as blue by comparison, and whenever a white pigment appears in exceedingly thin films against a black background, and its deviation from the true white by absorption disappears, another factor enters, the importance of which is, I believe, greatly underrated.

The increasing delicacy of the eye to the more refrangible rays of the spectrum as the light reaching the retina diminishes², comes powerfully into play in the case of these thin films, reinforcing an impression to which the judgment is already biased

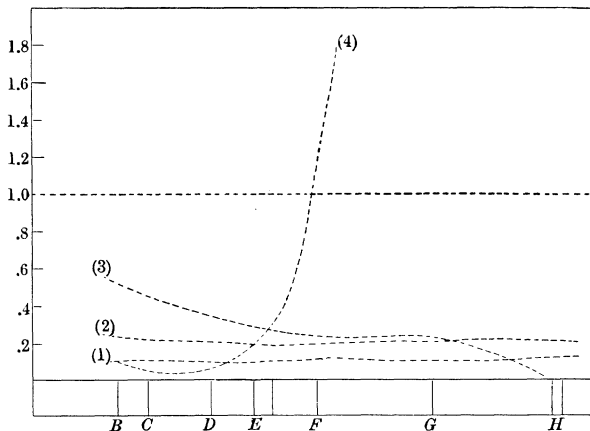


FIGURE IV.—Intensity curves of the spectrum of Sulphur precipitated from a solution Hyposulphite of Sodium.

(1) Reflexion spectrum in the incipient (blue) stage. (2) Reflexion spectrum in the "milky" stage. (3) Absorption spectrum of the solution in the "milky" stage. (4) Reflexion spectrum of artificial Ultramarine.

¹ Spectrophotometric Study of Pigments, Am. Journal of Science. Vol. 28.

² Albert; Wiedemann's Annalen. Vol. 16, p. 129.

by the real contrast already mentioned, until we accept as blue what is actually only a pure white of a very low degree of brightness.

Scarcely less important in photometry than the choice of our standard white, is the selection of a suitable black.

The ideal black, a substance which absorbs all wave-lengths completely, does not exist; and all blacks attainable in practice are simply pigments of very small reflecting power. A pure white of this kind would furnish what might appropriately be termed a *neutral* black, one, namely, which although possessed of some power of reflexion, would reflect all wave-lengths equally well.

The value of such a substance would be great, and would increase in proportion as its reflecting power was insignificant. All other blacks may be regarded simply as colored pigments of low brilliancy.

The superiority of lamp-black is so generally recognized, and its use in photometry so common, as to render it desirable to gain as accurate a knowledge as possible

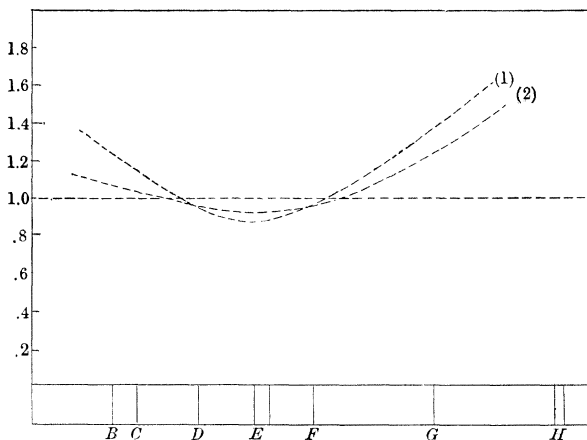


FIGURE V.—Intensity curves of the reflexion spectrum of two specimens of Lamp-black.

of the character of its spectrum. Its transparency to rays of the infra-red regions has long since been established, and its average reflective power for light has also been determined. Its spectrum, even when illuminated by direct sunlight, is so faint as to make its photometric analysis quite unsatisfactory, but the methods already applied

to other pigments were found sufficient to give a tolerable indication of its character. Fig. V shows the intensity curves of the spectrum of two specimens of lamp-black.

The deviations from the straight line, which would be characteristic of a neutral but imperfect black, are such as enable us to define lamp-black, not as a white of diminished brightness, but as a purple in which red is the dominant hue, but in which violet also greatly preponderates over the wave-lengths which form the central region of the visible spectrum. Fortunately, none of the visible rays reflected by this pigment are of sufficient intensity to prevent its adoption as the standard black in most spectrophotometric work, but the character of its intensity curves is such as to warrant the suspicion that black pigments will be found, upon analysis, to differ as widely from the ideal standard as do those substances which we are in the habit of regarding as white.

UNIVERSITY OF KANSAS, November, 1886.